Art. VI.—*Investigation of Waters and Saline Materials from Lake Eyre and District (Central Australia).*

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(Communicated by Professor A. C. D. Rivett.)

In July and August of 1922, a party, led by Mr. G. H. Halligan, F.G.S., of Launceston, Tas., journeyed to Marree, Northern South Australia, with the object of engaging upon the scientific investigation of the fauna and flora and geographical features of Lake Eyre and the district immediately surrounding it. The chief aim of the party was to launch a boat on North Lake Eyre itself, and then explore the area of open water which had been charted in an aeroplane survey, undertaken by Mr. Halligan, in the previous March.

Unfortunately, the project had to be abandoned owing to the recession of the water quite beyond the range of vision (about eight miles), leaving extensive mud flats, which it was impossible to cross at the only point where it had been thought feasible to launch the boat, namely, at the mouth of the Frome River, in the extreme south-eastern corner of the lake.

However, the party was able to get to the water in South Lake Eyre, and the samples were there collected. The analyses of these are given in this paper, together with those of other samples of material collected in the locality.

As a preliminary to this work, especially for the water analyses, it was deemed advisable to develop suitable analytical processes by working on samples of ordinary sea water. As a guide to the work, a series of analyses performed by Dittmar on the sea water samples collected by the " Challenger Expedition " and reported in " Challenger Reports," Vol. I., was consulted.

The investigations involved in this development and standardisation of methods, and the actual methods adopted are as follow :—

Analytical Procedure.

Chlorine.—The usual gravimetric procedure was followed. This gives chlorine and bromine combined.

Bromine.—A method of fractional precipitation with silver nitrate was employed. Chlorine was passed over the mixed silver chloride and bromide, and the bromide determined by the loss in weight due to the displacement of bromine by chlorine.

A litre of water was measured out, and about 30 c. cm. of 5N nitric acid was added. Then 1/25 of the amount of silver nitrate solution (220 c. cm. of N/10) necessary to precipitate all the halogen was added, and the mixture well shaken in a Winchester quart bottle. The precipitate was settled over-night. After de-

cantation, a further fractional precipitation was carried out with the same amount of silver nitrate. All the bromine was precipitated by the two fractionations. The washed precipitates were dried and placed in a porcelain boat in a small combustion furnace, the boat being contained in a small piece of combustion tubing about six inches long. Here the mixed halides were fused while a slow current of dry chlorine was passed over them, being led into the tube through a short piece of tube loosely ground into the end. Before passing chlorine, constant weight in a dry air current was obtained. Then constant weight was obtained in a dry chlorine current, the tube being finally washed out with air. In weighing, the boat was not disturbed, but was weighed in, and together with, the short combustion tube.

Results.

(For Ordinary Sea Water.)

No. of expt.	Weight of tube and boat after passing air.		Weight of tube and boat after passing chlorine.		Mean loss of weight.		Bromine per 100 g. of total salts.
A 2nd ppt. ..	48.5588	-	48.5534	-	0.0054	-	—
A 1st ppt. ..	48.6790	-	48.6525	-	0.0265	-	0.1586
B 2nd ppt. ..	46.8082	-	46.8033	-	0.0049	-	—
B 1st ppt. ..	46.7872	-	46.7548	-	0.0324	-	0.1854

The values given in column 5 were calculated from the losses in weight given in column 4, together with the following data:—

Weight of one litre of water -   -   -   -   1025.6g.
Weight of total salts per 100g. of water   -   3.53g.

Though done on samples collected at different times, these results showed too great a variation in the bromine content. They could not, however, be repeated, as the large volumes required for the determinations had used all of the samples available. Accordingly, some artificial sea waters were made up by dissolving 30g. of pure fused sodium chloride, and a definite weight (about 60 m.gm.) of bromine in the form of potassium bromide in one litre of distilled water. The sodium chloride was tested colorimetrically, and gave no indication of bromine. A blank determination was also run, using 30g. of sodium chloride, but no bromide.

No.	Air.	Chlorine.	Loss.		
Blank	46.8732 -	46.8730 -	Inappreciable.		
A 1st ppt. ..	40.0448 -	40.0153 -	0.0295 -	Equiv. to 0.0531 g. Br.	
A 2nd ppt. ..	39.5723 -	39.5692 -	0.0031 -	,, ,, 0.0056	,,
B 1st ppt. ..	37.9738 -	37.9438 -	0.0300 -	,, ,, 0.0540	,.
B 2nd ppt. ..	41.5844 -	Tube Cracked.			

Thus for experiment A, of 0.0605g. of bromine distributed through the solution (one litre) 0.0587g. were determined by the

method. For experiment B (using the second precipitate value of A, everything being under standard conditions) of 0.0590g. of bromine added 0.0596 were determined.

Thus, with careful manipulation, good results could be obtained.

Total Salts in Solution.—The first evaporations tried showed the necessity for weighing in a closed vessel owing to the hygroscopic character of the residue. Evaporations finished in the air even at 115-120°C. gave results too high, owing to non-expulsion of water of crystallisation.

e.g., A 3.64%   B 3.73%

Before becoming constant, A underwent a considerable number of dryings more than B. This leads to hydrolysis, so that the dried residues have to be dissolved in water and titrated for alkalinity with N/10 hydrochloric acid, and N/10 caustic soda, using methyl orange as indicator, and a form of " zig-zag " titration. This is more or less straightforward, but is tedious, and so are the subsequent calculations.

Two residues were transferred to porcelain crucibles, and heated over Meker burners to expel water of crystallisation, as mentioned above. These were rendered useless by volatilisation of some of the residue.

Evaporation in a current of dry hydrogen chloride gas (suggested by Prof. Rivett) was then undertaken. This proved very satisfactory, being easy in operation, and giving constant weights readily. No further corrections had to be made, as hydrolysis was entirely prevented, and the correction for conversion of carbonate into chloride was quite negligible. The results obtained were in good agreement, viz., 3.53% and 3.51%.

Further evaporations of 20 c. cm. samples in silica crucibles were undertaken. They were taken almost to dryness in the air oven at 115°C., heated just to a pink colour over a Bunsen burner for about five minutes, then cooled in a desiccator and the crucible weighed with the lid on. The residue was then removed and alkalinity determined by titration and calculation as before. The actual experimental work was, for the evaporation, about the same as in the case of the hydrochloric acid evaporation—if anything, somewhat less; but, after this, came the "zig-zag" titrations, and then the necessary calculations. These again proved tedious. The results were in fair agreement with those of the hydrochloric acid evaporation, being

3.53% and 3.56%.

The evaporation in a current of dry hydrochloric acid gas is, therefore, the best method for this determination.

Sulphate, Lime and Magnesia.—These were determined by the usual gravimetric methods as barium sulphate, calcium oxide (from oxalate), and magnesium pyrophosphate, respectively.

Total Bases as Sulphates.—Twenty c. cm. of water. were weighed into a silica crucible. 3 c. cm. of dilute sulphuric acid

(5N) were added, and the whole evaporated to dryness. Constant weight was obtained after alternate additions of more acid followed by evaporation and heating over a Meker burner for about fifteen minutes.

Carbonic Acid.—(By vacuum baryta method.) 300 g. of the sea-water were placed in a 700 c. cm. round-bottomed flask with side tube. In this flask the carbon dioxide was liberated by the addition of hydrochloric acid. The remainder of the apparatus, and the method of procedure, were similar to those given by G. Ampt., J. Soc. Chem. Ind. of Victoria, 1923, p. 1006. Dissolved gases in the water reduce the vacuum in the apparatus, but not sufficiently to impede the diffusion of the carbon dioxide into the absorption flask containing barium hydroxide.

Alkalis.—The mixed chlorides of sodium and potassium were obtained by the usual method (as given, for instance, in Mellor's " Quantitative Inorganic Analysis "). In these the potassium was then determined by precipitation as platinichloride.

Spectroscopic tests were carried out for the rarer alkali metals, a chart being prepared on which spectrum lines of known wavelengths, from known metals, were plotted against spectrometer readings.

Lake Eyre South Waters.

Analysis of Sample No. 1, collected in water 2 to $2\frac{1}{2}$ inches deep, 100 yards from the shore.

Specific gravity (20° C)	1.0581	
Hydrogen ion concentration (by polychrome indicator)	$10^{-7.5}$	
Total Salts	7.72	g. per 100 g. of water.
Total bases as sulphates	119.1	g. per 100 g. of total salts.
Calcium oxide	3.18	,, ,, ,, ,,
Magnesium oxide	0.66	,, ,, ,, ,:
Sodium oxide	47.84	,, ,, ,, ,,
Potassium oxide	0.476	,, ,, ,: ,,
Sulphur trioxide	5.31	,, ,, ,, ,,
Carbon dioxide	0.112	,, ,, ,, ,,
Chlorine	54.03	,, ,, ,, ,:
Chlorine minus basic oxygen	41.86	,, ,, ,, ,,
Bromine	0.015	,, ,, ,, ,,

Total bases as sulphates	120.1 Calculated.
,, ,, ,,	119.1 Found.

Summation of Constituents.   Equivalents

Summation of Constituents.			Basic.		Acidic.		
CaO	3.18	-					
MgO	0.66	-					
Na₂O	47.84	-					
K₂O	0.476	-	CaO	0.113	-		
SO₃	5.31	-	MgO	0.033	-	CO₂	0.005
CO₂	0.112	-	Na₂O	1.543	-	Cl	1.522
Cl-(O)	41.86	-	K₂O	0.010	-	SO₃	0.133
Br	0.015	-					
Total	99.46	-		1.699	-		1.660

Lithium, rubidium and caesium were proved by spectroscopic tests to be absent.

Sample No. 2, collected in water 3 inches deep, 200 yards from the shore.

Specific gravity (20° C) ..	1.0660	
Hydrogen ion concentration		
(by polychrome indicator)	$10^{-7.5}$	
Total salts	8.68	g. per 100 g. of water.
Total bases as sulphates ..	118.40	g. per 100 g. of total salts.
Calcium oxide..	2.66	,, ,, ,, ,,
Magnesium oxide	0.67	,, ,, ,, ,,
Sodium oxide	47.84	,, ,, ,, ,,
Potassium oxide	0.495	,, ,, ,, ,,
Sulphur trioxide	5.09	,, ,, ,, ,,
Carbon dioxide	0.110	,, ,, ,, ,,
Chlorine	55.74	,, ,, ,, ,,
Chlorine minus basic oxygen	43.18	,, ,, ,, ,,
Bromine	0.018	,, ,, ,, ,,

Total bases as sulphates ..	118.97	Calculated.
,, ,, ,, ..	118.40	Found.

Summation of Constituents				Equivalents.				
CaO ..	2.66	-						
MgO ..	0.67	-						
NaO ..	47.84	-		Basic.			Acidic.	
K_2O ..	0.495	-	CaO ..	0.095	-			
SO_3 ..	5.09	-	MgO ..	0.021	-	CO_2 ..	0.005	
CO_2 ..	0.110	-	Na_2O ..	1.543	-	Cl ..	1.560	
Cl–(O) ..	43.18	-	K_2O ..	0.011	-	SO_3 ..	0.120	
Br ..	0.018	-				-		
Total ..	100.06	-		1.670	-	·	1.685	

Lithium, rubidium and caesium were proved by spectroscopic tests to be absent.

Lake Eyre Materials.

Sample No. 1. Efflorescent material, obtained from an old well shaft sunk in shale.

Water soluble.. ..	89.50 %	
Moisture ..	47.07	
Calcium oxide ..	0.73	
Magnesium oxide ..	0.31	
Sodium oxide	17.84	Hydrogen ion concentration (by
Potassium oxide ..	0.34	polychrome indicator)
Sulphur trioxide ..	23.00	$10^{-9.2}$
Chlorine	1.00	
Chlorine minus basic		
oxygen	0.78	
Carbon dioxide ..	0.18	
Sum of soluble constituents	90.25	

The chief constituents, soda and sulphuric acid, are present in equivalent proportions, and it might be stated that of the total water-soluble matter 93% consists of sodium sulphate. This is interesting in view of the fact that the district abounds in gypsum ($CaSO_4.2H_2O$) and in salt ($NaCl$).

Sample No. 8. Saline scum from the lake margin.

Water soluble	84.82 %
Moisture	7.45
Calcium oxide	1.70
Magnesium oxide	0.94
Sodium oxide	36.80
Potassium oxide	0.20
Sulphur trioxide..	6.96
Carbon dioxide	0.092
Chlorine	39.66
Chlorine minus basic oxygen	30.70
Sum of soluble constituents	84.84